27 Hydrogenated Graphene
Preparation, Properties, and Applications

Tandabany C. Dinadayalane and Jerzy Leszczynski

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ABSTRACT

Graphene, a nanomaterial represented by a single atomic layer of planar carbons, continues to attract widespread research interest due to its remarkable electronic and structural properties. Chemical modification of graphene includes attachment of atomic hydrogen to selected carbon sites or all carbon sites correspondingly produces partially hydrogenated graphene (PHG) or fully hydrogenated graphene (graphane). H chemisorption is accompanied by transformation of carbon from sp² to sp³ hybridization, resulting in a relaxation of the carbon atom toward the hydrogen atom. In this chapter, we reveal different approaches used for hydrogenation of graphene, and various experimental techniques employed for the characterization of structures, dehydrogenation, and important properties of hydrogenated graphene. We outline four isomeric single-sheet graphanes. Theoretical and experimental studies focusing on the feasibility of single-sided hydrogenated graphene at both low and high hydrogen coverage are delineated. We discuss the electronic and mechanical properties of graphane and PHG. The results of vibrational spectra and nuclear magnetic resonance (NMR) data from computational studies are provided. We also highlight the recent studies of experimentally known fluorographene, partially hydrogenated graphene (C₄H), graphane nanotubes, and bilayer graphane. As an emerging and important field, the fully hydrogenated derivative of graphene (called graphane) and PHG have many potential applications and deserve detailed review of their characteristics and further comprehensive studies.

27.1 INTRODUCTION

The electronic structure of graphene as a two-dimensional (2D) atomic sheet of carbon was predicted in 1947. However, the first experimental synthesis and characterization of graphene was reported in 2004 by Novoselov et al. In the last decade, graphene stimulated vast interest due to its outstanding electrical, thermal, and mechanical properties. Graphene is considered an important material for many next-generation technologies, including high-frequency electronics, broadband photodetectors, supercapacitors, biological and gas sensors, alternative energy, etc. It has applications in a wide range of research areas such as chemistry, physics, biology, materials science, and medicine. The 2010 Nobel Prize in Physics to Geim and Novoselov validates the importance of graphene not only in basic research but also in various commercial applications. There have been many reviews on graphene and its potential applications in recent years. Hence, in this chapter, we do not discuss graphene but we focus on partially hydrogenated graphene (PHG) and fully hydrogenated graphene (graphane), which represents an important functionalized graphene derivative.
Covalent functionalization of carbon nanomaterials, particularly carbon nanotubes and graphene, has been mainly employed to increase the solubility of these materials. Sidewall covalent functionalization of single-walled carbon nanotubes (SWCNTs) using different functional groups has been studied in our group. Importantly, we have investigated the chemisorption of one and two hydrogen atoms with SWCNTs using density functional theory (DFT) calculations. In case of carbon-based nanomaterials, chemisorption of hydrogen atoms is accompanied by a change in hybridization of the carbon atoms from $sp^2$ to $sp^3$.

The chemisorption of hydrogen is an efficient way to modify the electronic properties of graphene because of its small volume and large contact area. Experimental investigation supported by Raman spectroscopy and transmission electron microscopy (TEM) revealed that hydrogenation of single-layer graphene (SLG) dramatically changes the electronic and transport properties, as well as the atomic structure of graphene. The chemisorption of hydrogen atoms on graphene induces magnetic moments in the system. Using DFT calculations, Boukhvalov et al. studied the electronic structure, magnetic properties, and energetics of different hydrogenated graphene layers. At low hydrogen coverage, the chemisorbed H atoms behave like defects in $sp^3$ C=C matrix. On the other hand, at high hydrogen coverage, the $sp^3$ C−H bonds become coalescent clusters resulting in a confinement effect on the $sp^2$ C domains. The region of structural distortion caused by C−H bonding was predicted in the range of a few atoms around the hydrogenation site, which is much smaller than 1 nm. Hydrogen chemisorption is occasionally called hydrogen passivation of graphene. In vitro toxicological assessments were reported for highly hydrogenated graphene and graphene oxide. Previous works on graphene and graphene-based nanomaterials published in the literature are summarized in Table 27.1.

### 27.2 STRUCTURE OF GRAPHANE

It is well known that hydrocarbons are the simplest organic compounds and they consist only of carbon and hydrogen atoms. In general, hydrocarbons are molecules consisting of a carbon backbone with hydrogen atoms attached. The backbone can be a linear chain, a ring, or combination of both. Sofo et al. predicted the structure of graphene as an extended 2D covalently bonded hydrocarbon. They revealed that graphene is a semiconductor. Their theoretical study based on first-principles total-energy calculations motivated the experimental search for graphene. Two years later, Elias et al. reported the experimental evidence for novel extended 2D hydrocarbon of graphene.

Chair and boat configurations of fused cyclohexane rings were predicted to be energetically favorable for graphene. In the chair configuration of graphene, the C−C bond connects carbon atoms with hydrogen attached at opposite sides of the plane. In this case, the length of C−C bond was calculated as 1.52 Å that is comparable to the C−C bond length of 1.53 Å in diamond.

### Table 27.1

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Thus, the graphene structure is similar to the diamond structure since the carbon atoms have the same type of bonds. It should be noted that the boat configuration of graphene has two different types of C−C bonds: the first type of C−C bond has a bond length of 1.52 Å and the hydrogen atoms attached to these carbons are on opposite sides of the plane, and the second type of C−C bond has a bond length of 1.56 Å and the hydrogen atoms attached to these carbons are on the same side of the plane. The slightly longer bond length for the latter case than for the former one could be attributed to H···H repulsion; thus, the boat configuration is not as stable as the chair configuration. For both chair and boat configurations of graphene, the C−H bond length was found to be the same (1.1 Å). It should be noted that the C−C bond distance in graphene is 1.42 Å. For fully hydrogenated graphene, Boukhvalov et al. reported a C−C bond length of 1.526 Å and a C−H bond length of 1.110 Å, and the bond angles of 102.8° and 107.5° correspondingly for C−C and C−H. The stability of chair, boat, and twist-boat graphene structures was examined using first-principles density functional theory calculations (Table 27.2).

Figure 27.1 also depicts four isomeric 2D sheets of stoichiometry CH, labeled i–iv. The isomers i and ii have a chair configuration, while iii and iv have a boat configuration. All these four isomers were reported to be stable. Hoffmann and coworkers have mentioned that many other isomeric graphene sheets are practically plausible. They have also demonstrated the ways to construct different isomers. They could not obtain the isomer with all hydrogen atoms on one side because such a structure is highly strained. The factors controlling the stability of saturated hydrocarbons like isomers i–iv of graphene are well known in organic chemistry—they include (1) CCC angles, (2) eclipsing and staggering interactions along
the C—C bonds, and (3) through-space steric interactions of hydrogen atoms. Based on simple organic chemistry rules and without doing any calculations, one would expect that i and ii (chair cyclohexanes) are more stable than iii and iv (boat cyclohexanes). Moreover, ii is less stable than i because ii has some close H···H contacts between nearby cyclohexane rings. Calculated energies confirmed this expected ordering (see Figure 27.2).

The formation energy with respect to other competing hydrocarbons is important from a synthetic point of view. The values of formation energy per atom for different hydrocarbons shown in Figure 27.2a indicate that graphane lies in the group of already-known and highly stable hydrocarbons such as polyethylene, benzene, cyclohexane, cyclohexene, and methane. As shown in Figure 27.2b, the benzene molecule and the trans- and cis-polyacetylene structures are reported to be less stable than the different isomeric structures i–iv of graphane.42 A study concerning various stable crystal structures of graphane revealed that locally stable twist-boat membranes significantly contribute to the experimentally observed lattice contraction.41

### 27.3 PREPARATION AND CHARACTERIZATION OF HYDROGENATED GRAPHENE

Graphene is well known for its high thermodynamic stability and chemical inertness. Therefore, new methods and techniques are required to create covalent bonds without any unwanted side reactions or irreversible damage to the graphene sheet.3 Chemisorption of hydrogen on sp$^2$-hybridized carbon network is an interesting area of research since it modifies the electronic structure of the carbon networks. Theoretical studies predicted that the product of complete, one side hydrogenation of graphene is thermodynamically unstable.31,39 Several techniques have been explored for effective and controllable hydrogenation of graphene.37 Experimental study demonstrated that graphene or hydrogenated graphene can be prepared by the hydrogenation and unzipping of SWCNT.43 Interestingly, graphene was prepared by the irradiation of graphene having H$_2$O adsorbates on both sides of the graphene layer. It is important to mention that PHG was formed by the irradiation of graphene having H$_2$O or NH$_3$ adsorbates on only one side of the layer.44

Hydrogenated graphene has been produced primarily using two techniques: (1) atomic hydrogen beams, in which molecular hydrogen is cracked on a hot filament26,30,37 and (2) exposure to hydrogen-based plasmas.27,29,36,45 In general, atomic hydrogen beams are utilized for producing graphene with low coverage of hydrogen, while hydrogen plasmas provide sufficient hydrogen atoms to realize graphane. It is important to highlight that hot, high-power plasmas result in

<table>
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<tr>
<td>Chair configuration</td>
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<tr>
<td>Boat configuration</td>
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Note: Bond distances are given in Å. The C—C (sp$^3$-hybridized C atoms) bond length in diamond is 1.53 Å. The C—C bond distance in graphene is 1.42 Å.39

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hydrogenated graphene with significant irreversible defects. Nevertheless, low-temperature plasmas and atomic hydrogen beams add hydrogen in a manner that is thermally reversible to pristine graphene. Hydrogenation of graphene by an Ar/H\textsubscript{2} plasma produced in a reactive ion etching (RIE) system can lead to a high and fast hydrogen uptake. Furthermore, it does not require special sample preparation and is compatible with microfabrication techniques.\textsuperscript{27}

Wojtaszek et al. revealed that hydrogenation of graphene happens primarily due to the hydrogen ions and not due to highly accelerated plasma electrons fragmenting the water add-layer on the graphene surface as suggested by Perez et al.\textsuperscript{27,46} Hydrogenation of graphene was performed by the chemical reaction of SLG with hydrogen atoms, generated \textit{in situ} by the electron-induced dissociation of hydrogen silsesquixoxane (HSQ).\textsuperscript{47} Experimental studies used e-beam lithography for hydrogenation with single- and multilayer graphene.\textsuperscript{44,47} Byun et al. studied the nanoscale hydrogenation of graphene under normal atmospheric conditions and at room temperature without etching, wet process, or even any gas treatment by controlling just an external bias through atomic force microscope (AFM) lithography. Micro-Raman spectroscopy was used to confirm the nanoscale hydrogenation of graphene.\textsuperscript{48}

Balog et al. have reported the chemisorption of atomic hydrogen on graphene experimentally. At low hydrogen coverage, the formation of hydrogen dimer (two hydrogen atoms present at \textit{ortho} positions and two hydrogen atoms present at \textit{para} positions) was confirmed by scanning tunneling microscopy (STM) images. Figure 27.3 shows an STM image of the graphene sample after hydrogen exposure. A number of bright protrusions are observed due to chemisorption of hydrogen atoms. Hydrogenation was shown to be reversible by thermal annealing.\textsuperscript{49} It is important to mention here that experimental studies on hydrogenation of mono-, bi-, tri-, and multilayer graphene have been reported.\textsuperscript{26,45,50} Elias et al.\textsuperscript{26} and Ryu et al.\textsuperscript{47} independently demonstrated that hydrogenation is more feasible on SLG than that on bilayer graphene (BLG). Some other studies concluded that bilayer and multilayer graphene are quite susceptible to chemisorption of hydrogen atoms despite a stiffer lattice structure.\textsuperscript{45,50} Different techniques used for producing graphene or PHG are listed in Table 27.3.

Guisinger et al. have utilized STM and scanning tunneling spectroscopy (STS) in their study on chemisorption of hydrogen with graphene on SiC surface.\textsuperscript{37} Pairwise adsorption of H atoms was observed on the graphene surface, with a subtle long-range effect on the electronic structure. The two most energetically favorable configurations for hydrogen pair formation are (a) two hydrogen atoms that are on opposite sides of the hexagonal ring or (b) they are adjacent. Unlike graphite, chemisorption of hydrogen atoms with graphene showed dramatic change in the local density of states (LDOS) over a spatial region much larger than the atomic adsorption sites.\textsuperscript{37} STS was used to probe the electronic information of the surface that is related to the LDOS.\textsuperscript{30}

Very recently, Scheffler et al. have studied hydrogenated, quasi-freestanding graphene by means of high-resolution STM and STS. They also used first angle-resolved photo-emission spectroscopy (ARPES) to provide evidence for the

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**FIGURE 27.2** (a) Formation energy per atom as a function of hydrogen content in atomic percent. Graphane is among the most stable hydrocarbons and it is the most stable for its hydrogen concentration. It is also more stable than mixtures of cyclohexene and graphite. Calculated binding energy of 9.55 eV/atom for graphite and 3.27 eV/atom for H\textsubscript{2} was used. (Reprinted with permission from Sofo, J. O., Chaudhari, A. S., and Barber, G. D. Graphane: A two-dimensional hydrocarbon. \textit{Phys. Rev.} B, 75, 153401. Copyright 2007 by the American Physical Society.) (b) The relative energy (in eV per CH, relative to single-sheet graphane i, 0 K) of some CH structures. (Wen, X.-D. et al., Graphane sheets and crystals under pressure. \textit{Proc. Natl. Acad. Sci. USA}, 108, 6833–6837, Copyright 2011 National Academy of Sciences, U.S.A.)
Hydrogenated Graphene

The preferential hydrogen adsorption patterns on graphene and the local electronic structure of H impurities have been explored. Since hydrogen impurities tend to have high mobility, the mapping of the hydrogen spots with an STM tip was performed with particular conditions, such as low bias and slow scanning speed. Figure 27.4 shows representative atomic-resolution topography images of the hydrogenation sites, and the structures with charge density distributions obtained from density functional tight-binding (DFTB)-based calculations for single and double hydrogenation with graphene.

Estimation of hydrogen chemisorption on graphene using STM has certain limitations: (a) STM probes the surface only locally and (b) the measurements are time consuming and difficult when graphene is deposited on the insulating substrate. Raman spectroscopy is considered an alternative approach because it is a relatively easy, nondestructive, noncontacting, and quick method to estimate hydrogen coverage from even micrometer-sized samples. More importantly, it can be used at room temperature and atmospheric pressure. Jaiswal et al. investigated the electronic properties of graphene sheets and graphene nanoribbons (GNRs) with different degrees of hydrogenation using a combination of charge transport and Raman spectroscopy experiments.

Elias et al. first annealed all graphene samples at 300°C in an argon atmosphere for 4 h in order to remove any possible contamination. Later, the samples were exposed to cold hydrogen plasma. A low-pressure (0.1 mbar) hydrogen–argon mixture (10% H₂) with direct current (DC) plasma ignited between two aluminum electrodes. Two hours of plasma treatment were required to reach saturation. The hydrogenated samples were stable at room temperature for many days and showed the same characteristics during repeated characterization measurements. The original metallic state was restored by annealing using 450°C in Ar atmosphere for 24 h. It should be noted that the higher annealing temperature damaged the graphene. After the annealing, the sample returned practically to the same state as before hydrogenation. It is important to note that standard methods like thermal programmed desorption (TPD), which is used for graphite, are insensitive to the possible amounts of desorbed hydrogen from micro-sized flakes.

### TABLE 27.3

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Technique for Preparation</th>
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<td>1</td>
<td>Hydrogenation and unzipping of SWCNT</td>
<td>Graphane</td>
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<td>2</td>
<td>Irradiation of graphene having H₂O adsorbates on both sides</td>
<td>Graphane</td>
<td>44</td>
</tr>
<tr>
<td>3</td>
<td>Irradiation of graphene having H₂O or NH₃ adsorbates on one side</td>
<td>PHG</td>
<td>44</td>
</tr>
<tr>
<td>4</td>
<td>Atomic hydrogen beam e-Beam lithography</td>
<td>PHG</td>
<td>26,30,37</td>
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<td>Hydrogen-based plasmas Hyogenation with single- and multilayer graphene</td>
<td>Graphane</td>
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<td>44,47</td>
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<td>7</td>
<td>Chemisorption of atomic hydrogen</td>
<td>PHG and/or</td>
<td>47,49</td>
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<td></td>
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<td>graphene</td>
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A wide range of characterization techniques, including scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS), Fourier-transform infrared spectroscopy (FTIR), x-ray photoelectron spectroscopy (XPS), combustion elemental analysis, energy-dispersive x-ray fluorescence spectroscopy (ED-XRF), near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, inductively coupled plasma optical emission spectroscopy (ICP-OES), Raman spectroscopy, photoluminescence measurements, and electrical resistivity measurements is available. More than one or two techniques are generally used to confirm the hydrogenation of graphene. Raman spectroscopy has been widely applied for the investigation of covalently functionalized graphene. It is very useful to understand structural and electronic properties of graphene/hydrogenated graphene, including layer numbers, stacking order, strain effect, and doping concentration. It has been utilized in characterizing hydrogenation of graphene. Two important peaks in the Raman spectra for carbon-based materials are the G and D peaks that lie around 1580 and 1350 cm\(^{-1}\), respectively. The G peak corresponds to optical \(E_{2g}\) phonons at the Brillouin zone center, whereas the D peak is caused by breathing-like modes (corresponding to transverse optical phonons near the K point). Both the G and D peaks arise from vibrations of \(sp^2\)-hybridized carbon atoms. It is worth mentioning that the D peak intensity provides a convenient measure for the amount of disorder in graphene. Its overtone, the 2D peak, appears around 2680 cm\(^{-1}\) and its shape identifies monolayer graphene. The 2D peak may even appear in the absence of any defects because it is the sum of two phonons with opposite momentum.

Figure 27.5 shows the changes in Raman spectra of graphene caused by hydrogenation: (a) hydrogenation of graphene on \(SiO_2\) surface and (b) hydrogenation of freestanding graphene. The D peak in hydrogenated graphene is observed at 1342 cm\(^{-1}\) and is very sharp, as compared to that in disordered or nanostructured carbon-based materials. This sharp D peak was reasoned to the breaking of the translational symmetry of C–C \(sp^2\) bonds after the formation of C–H \(sp^1\) bonds in hydrogenated graphene. In Figure 27.5, the peak that appeared at \(\approx 1620\) cm\(^{-1}\) corresponds to D'. After annealing, the Raman spectrum recovered to almost its original shape corresponding to graphene. Other recent experimental studies have also confirmed the above-mentioned peaks for hydrogenated graphene. It should be noted that the D peak could become up to three times greater than the G peak after prolonged exposures of graphene to atomic hydrogen. Recently, Hirsch et al. have mentioned that highly hydrogenated graphene material exhibited two very broad bands between 1000 and 3000 cm\(^{-1}\) covering the complete D, G, and 2D band regions. It should be noted that the D, G, and 2D bands of hydrogenated graphene showed significant dependence on hydrogen coverage as well as on excitation energies. Thus, they provide valuable information on the structural and electronic properties of graphene with increasing hydrogen coverage.

Very recently, Eng et al. have prepared highly hydrogenated graphene containing 5 wt.% of hydrogen by means of Birch reduction of graphite oxide using elemental sodium in liquid \(NH_3\) as electron donor and methanol as proton donor in the reduction. Schafer et al. have reported hydrogenation of graphene using a Birch-type reduction by the use of water as the hydrogen source. They have used IR spectroscopy in...
Hydrogenated Graphene

27.4 ELECTRONIC TRANSPORT PROPERTIES

The quantum electronic transport in low-dimensional disordered systems has been the subject of extensive studies for over several decades. Graphene is a zero band gap semimetal. However, hydrogenated graphene was proved to exhibit a semiconducting nature of strong temperature dependence (\(\Delta R/\Delta T < 0\)).\(^{26,28,29}\) Figure 27.6 shows the changes of electronic properties of graphene by hydrogenation. The metallic dependence close to the neutrality point (NP) (near zero gate voltage, \(V_g\)) below 50 K and the half-integer quantum Hall effect (QHE) at cryogenic temperatures (Figure 27.6b) are well-known characteristics of SLG. Chemisorption of atomic hydrogen with graphene exhibited an insulating behavior such that the resistivity (\(p\)) grew by two orders of magnitude with decreasing temperature (\(T\)) from 300 to 4 K. The quantum Hall plateaus, which were observed in the original graphene system, completely disappeared, with only weak signatures of Shubnikov–de-Haas oscillations remaining in magnetic field \(B\) of 14 T (Figure 27.6d). Vacancies induced by plasma damage or residual oxygen during annealing could be the reasons for the shift and change of peaks given in Figure 27.6f compared with Figure 27.6b. Low-temperature measurements revealed that the transport enters a variable range hopping regime in the heavily hydrogenated samples, but the full description of this transition is still lacking.\(^{26}\)

their recent study for the characterization of hydrogenated graphene samples. As shown in Figure 27.5c, two sharp bands at 3676 and 3566 cm\(^{-1}\) correspond to free hydroxyl and amino groups introduced in side reactions. The broad signal obtained at 2852 cm\(^{-1}\) is characteristic for C–H vibrations.\(^{17}\) Eng et al. have confirmed the successful hydrogenation of graphene by IR frequencies at 2850 and 2950 cm\(^{-1}\) corresponding to C–H stretching.\(^{35}\) XPS has also been used in the recent investigations of hydrogenated graphene.\(^{17,35,45}\) It should be noted that hydrogen cannot be detected by XPS. However, two differently bonded carbon atoms in the hydrogenated sample were identified. NEXAFS spectroscopy was used to characterize the hydrogenation of SLG grown on Pt(111), Ir(111), and Ni(111) surfaces.\(^{55}\) The polyhydrogenated graphene (phG) was characterized by AFM. The presence of a band gap and the change in electronic properties induced by the high degree of functionalization explain the fluorescence observed for phG. Solid-state cross-polarization magic-angle spinning (CP-MAS) \(^{13}\)C nuclear magnetic resonance (NMR) spectroscopy has also been used for the verification of hydrogenated graphene. The \(^{13}\)C NMR peaks obtained at 130 and 44.3 ppm were assigned to the \(^{13}\)C\(_{sp2}\) atoms and \(^{13}\)C\(_{sp3}\)H centers.\(^{17}\)

The dehydrogenation of hydrogenated graphene layers starts at temperatures as low as 75–100°C and this process can be completed at 350°C with a long annealing duration. It is interesting to note that in case of hydrogenated graphene samples with low hydrogen coverage, when the samples are annealed with the temperature around 175–200°C, the residual defects cannot be thermally healed with an annealing temperature below 200°C. Luo et al. revealed that there are two types of dehydrogenation mechanisms with dissimilar dehydrogenation barriers, which exhibit different dependencies on the number of graphene layers and the amount of hydrogen coverage.\(^{45}\) Computational study based on time-dependent DFT demonstrated the usefulness of short laser pulses for efficient and selective hydrogen removal from the upper or lower side of graphene.\(^{56}\)

Figure 27.5 (a and b) Changes in Raman spectra of graphene caused by hydrogenation. The spectra are normalized to have a similar intensity of the G peak. (a) Graphene on SiO\(_2\). (b) Freestanding graphene. The curves from top to bottom correspond to pristine, hydrogenated, and annealed samples. graphene was hydrogenated for approximately 2 h, and the spectra were measured with a Renishaw spectrometer at wavelength of 514 nm and low power to avoid damage to the graphene during measurements. (Left inset) Comparison between the evolution of D and D' peaks for single- and double-sided exposure to atomic hydrogen. Shown is a partially hydrogenated state achieved after 1 h of simultaneous exposure of graphene on SiO\(_2\) (bottom curve) and of a membrane (top curve). (Right inset) TEM image of one of the membranes that partially covers the aperture 50 mm in diameter. ((a and b) From Elias, D. C. et al. Control of graphene’s properties by reversible hydrogenation: Evidence for graphane. Science 2009, 323, 610–613. Reprinted with permission of AAAS.) (c) IR spectra of polyhydrogenated graphene (phG) and polydeuterated graphene (pdG). (d) AFM image of polyhydrogenated graphene (phG). ((c and d) Schafer, R. A.: On the way to graphene—Pronounced fluorescence of polyhydrogenated graphene. Angew. Chem. Int. Ed. 2013. 52. 754–757. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)
Matis et al. have reported the n-type nature of hydrogenated graphene on a SiO$_2$ substrate as well as the first demonstration of the complete reversibility of the majority carrier type using surface adsorbates (e.g., water). They indicated that hydrogenation of graphene induced a band gap by temperature-dependent electronic transport measurements. Moreover, the band gap reached a maximum value at the charge neutrality point (CNP) in the moderate temperature region of 220–375 K. It could be altered by an electric field effect and influenced by hydrogen coverage with graphene. Hydrogenated graphene material is increasingly n-type for increasing levels of hydrogenation. Although the hydrogenated film was shown to behave as n-type material, the incorporation of water physisorbed on the surface changed the material to p-type (Figure 27.6g). The adsorbed water molecule is a known electron donor. It is important to gain knowledge on the role of different H coverage of graphene on electronic transport and to be able...
to control this process. Sessi et al. pointed out that individual hydrogen adsorption sites can have a dramatic effect on the electronic properties of graphene.\textsuperscript{30} Depending on the H coverage, one can alter the transport properties of graphene from metallic to semiconducting and ultimately to an insulating state by full hydrogenation of graphene (graphane).\textsuperscript{26,29,57} Wojtaszek et al. have measured the electronic transport for the hydrogenation of SLG and BLG. BLG exhibited a monotonic increase of resistivity with increasing Ar/H\textsubscript{2} plasma exposure time, whereas for SLG, a nonmonotonic change in resistivity was observed, suggesting a change in the transport mechanism for exposure time more than 30 min.\textsuperscript{27}

The formation of midgap states is a consequence of hydrogen chemisorption with graphene. For PHG, the temperature-dependent transport in the midgap states shows a weak insulating behavior.\textsuperscript{50} In agreement with the theoretical estimates on short-range scattering,\textsuperscript{58} the experimental results of the conductivity of PHG showed close to linear dependence on carrier density away from the NP.\textsuperscript{50} Jaiswal et al. observed similar changes in electronic properties of graphene sheet and parallel GNRs upon chemisorption of hydrogen atoms.\textsuperscript{50} Previous investigations on heavily hydrogenated monolayer graphene have demonstrated the suppression of magnetoconductance oscillations.\textsuperscript{26} Jaiswal et al. have also examined the transport properties of PHG under a magnetic field. Both parallel GNRs and bulk graphene exhibited comparable modulation of transport properties upon hydrogenation. In principle, it may be possible to tune the electronic state of the system from an insulator to a quantum Hall conductor using magnetic field-induced delocalization by precisely controlling the fraction of hydrogenated sites and a very high magnetic field.\textsuperscript{50}

### 27.5 THEORETICAL STUDIES OF HYDROGENATED GRAPHENE

#### 27.5.1 Structures and Binding Energies

Bulat et al. examined the relative reactivities of different sites of two model graphene systems, namely, coronene (C\textsubscript{24}H\textsubscript{12}) and circumcoronene (C\textsubscript{54}H\textsubscript{18}) by low hydrogen as well as fluorine chemisorption (Figure 27.7a and b).\textsuperscript{59} They utilized DFT at B3LYP/6-311G(d,p) level for computing the reaction energies for addition reactions and to verify the prediction of reactivity based on the average local ionization energy, I\textsubscript{S}(r).

![Figure 27.7](image)

**FIGURE 27.7** (See color insert.) (a) Computed I\textsubscript{S}(r) on the 0.001 au molecular surface of coronene (C\textsubscript{24}H\textsubscript{12}) and circumcoronene (C\textsubscript{54}H\textsubscript{18}). Light blue circles denote the positions of the I\textsubscript{S}(r) minima, I\textsubscript{S,min}. Color ranges, in eV, are as follows: blue, less than 10.1; green, from 10.1 to 11.1; yellow, from 11.1 to 12.1; red, greater than 12.1. (b) Structures of monofunctionalized (by H or F) coronene (C\textsubscript{24}H\textsubscript{12}X) and circumcoronene (C\textsubscript{54}H\textsubscript{18}X) with different positions numbered where second H or F was attached. (a) and (b) Reprinted with permission from Bulat, F. A. et al. Hydrogenation and fluorination of graphene models: Analysis via the average local ionization energy. J. Phys. Chem. A, 116, 8644–8652. Copyright 2012 American Chemical Society.) (c) Structures of larger graphane-like H clusters on graphene on Ni and Pt surface, and on freestanding graphene at various % of H coverage. On freestanding graphene, H atoms attached from below (above) are shown in yellow (red). Binding energies per H atom are given in eV using M06-L and PBE. (d) Binding energies per H atom as a function of coverage for graphane-like H clusters (connected dots) and ortho-dimers (stars) on graphene adsorbed on Ni (left) and on Pt (right). The two series shown are calculated with M06-L (black line) and PBE (dashed gray line). (c) and (d) Reprinted with permission from Andersen, M., Hornekær, L., and Hammer, B. Graphene on metal surfaces and its hydrogen adsorption: A meta-GGA functional study. Phys. Rev. B, 86, 085405-1–085405-6. Copyright 2012 by the American Physical Society.)
Their detailed computational study reveals that the edges of graphene sheets are more reactive than the interior portions. In case of addition of two hydrogen or fluorine atoms, the ortho products are the most stable and the meta products are the least stable. It should be noted that the para addition is sometimes competitive with or even greater than the ortho addition.\textsuperscript{59}

Hydrogenation of the freestanding graphene and the graphene on Ni and Pt metal surfaces was studied using the DFT method.\textsuperscript{60} The widely used meta-generalized gradient approximation (MGGA) functional of M06-L was employed for the calculations and the results obtained using M06-L and Perdew–Burke–Ernzerhof (PBE)\textsuperscript{61} functionals were compared. The influence of metal surface on the hydrogen chemisorption of graphene was examined by focusing on mono H addition, positional preference for ortho, meta, and para additions of two H atoms. The comparison of the results obtained with the M06-L and PBE functionals suggested the importance of using a functional that is capable of accurately describing the graphene–metal interactions. The PBE functional produced significant error at low H coverage and for the case of a strongly interacting Ni substrate. For graphene on a Ni surface, the binding energies per H atom are almost constant with increasing H coverage. However, in case of graphene on a Pt surface, the binding energies per H atom increase with increasing H coverage (see Figure 27.7d).\textsuperscript{60}

DFT calculations with PW91/DNP (implemented in the DMol3 program)\textsuperscript{62,63} were used to understand the electronic structures of hydrogenated graphene with different configurations.\textsuperscript{64} DNP is nothing but double numerical basis, including d- and p-polarization function. Fully hydrogenated graphene (graphane) on two sides in the chair-like configuration was considered because of the following two reasons: (1) the chair-like configuration is more stable than the boat-like configuration and (2) the chair-like graphene possesses higher symmetry than the boat-like configuration and is able to remove adjacent H atoms in pairs on two sides of the sheet. A large orthogonal supercell (12 × 10 rectangular unit cells) containing 240 carbon atoms and 240 hydrogen atoms (C\textsubscript{240}H\textsubscript{240}) was used in that study. PHG (or dehydrogenated graphane) configurations were constructed by removing hydrogen atoms from a perfect graphene. Although there are other ways of generating PHG configurations, three types were considered by Gao et al.: (1) randomly removing H pairs from fully hydrogenated graphene, (2) randomly removing individual H atoms from fully hydrogenated graphene, and (3) creating paired H vacancies according to some ordered pattern.\textsuperscript{64}

Gao et al. considered a series of hydrogenated graphene with H coverage of 95.8%, 91.7%, 87.5%, 83.3%, 79.2%, 75%, 70.8%, and 66.7%, corresponding to C\textsubscript{240}H\textsubscript{230}, C\textsubscript{240}H\textsubscript{220}, C\textsubscript{240}H\textsubscript{210}, C\textsubscript{240}H\textsubscript{200}, C\textsubscript{240}H\textsubscript{190}, C\textsubscript{240}H\textsubscript{180}, C\textsubscript{240}H\textsubscript{170}, and C\textsubscript{240}H\textsubscript{160} in the supercell model. They also considered systems with H coverage of 62.5% (C\textsubscript{240}H\textsubscript{150}), 50% (C\textsubscript{240}H\textsubscript{120}), 37.5% (C\textsubscript{240}H\textsubscript{90}), 25% (C\textsubscript{240}H\textsubscript{60}), and 12.5% (C\textsubscript{240}H\textsubscript{30}). Figure 27.8 depicts the representative structures of PHG, the graph of hydrogen binding energies as the function of H coverage, and the plot showing the changes of energy gap of hydrogenated graphene as a function of H coverage.\textsuperscript{64} The stability of hydrogenated graphene as a function of H coverage was described by the binding energy \( E_b \) of hydrogen atoms, which is defined as

\[
E_b(n) = \frac{(E_{\text{graphene}} + nE_H - E_{\text{PHG}})}{n}
\]

where \( E_{\text{graphene}} \) and \( E_{\text{PHG}} \) are the total energies of the pristine graphene and the PHG adsorbed with \( n \) hydrogen atoms, respectively, and \( E_H \) is the total energy of an isolated H atom.\textsuperscript{64} The computed binding energy of the perfect graphene is 2.59 eV/H, which is close to a theoretical value of 2.54 eV/H at PBE/6-31G** level using the Gaussian 03 program. For PHG with both kinds of H vacancies (paired or unpaired), the hydrogen binding energy was shown to decrease as the H coverage decreased. The paired vacancies are energetically more favorable than unpaired H vacancies at the same H coverage (Figure 27.8f). The hydrogen binding energy of the hydrogenated graphene is higher than that of the H\textsubscript{2} molecule for the hydrogen coverage range of 66.7%–100%. The computational study concluded that the formation of PHG with sufficiently high H coverage from gaseous H\textsubscript{2} molecules and graphane is exothermic.\textsuperscript{64} The presence of physisorbed polar hydride molecules, such as H\textsubscript{2}O, HF, and NH\textsubscript{3} that work as a shuttling catalyst greatly assists for the facile hydrogenation of graphene.\textsuperscript{65}

### 27.5.2 Band Gap and NMR Chemical Shifts

Karlický et al. collected and listed from the literature the band gap values for graphane and fluorographene at different computational levels using a range of software. The band gap values were computed using LDA, PBE, BPW91, BLYP, TPSS, M06-L, and HSE06 functionals in conjunction with various basis sets (Pople's double-\( \zeta \) and triple-\( \zeta \), as well as Dunning's correlation consistent basis sets). The results obtained using different levels were compared with those of the projector augmented waves method with plane-wave basis sets implemented in the Vienna \textit{ab initio} simulation package (VASP).\textsuperscript{66} The band gap values of 5.4 eV for the stable chair configuration and 4.9 eV for the metastable boat configuration were reported using GW approximation (GWA) of Hedin.\textsuperscript{67} The approximation is the expansion of the self-energy \( \Sigma \) in terms of the single particle Green's function G and the screened Coulomb interaction W. The computed value for the chair configuration of graphane (5.4 eV) is comparable to that of diamond crystal with full sp\textsuperscript{3} hybridization (5.48 eV). However, the calculations using generalized gradient approximation (GGA) yielded the value of 4.66 eV for the perfect graphene. Appropriate pairwise dehydrogenation of graphene changes insulating graphene to a semiconductor. Gao et al. mentioned that paired H vacancies are necessary to achieve a clean band gap without midstates in the PHG. GGA calculations showed the reduction of band gap of 4.66 eV for a fully hydrogenated graphene to zero for the PHG with 66.7% H coverage (Figure 27.8g).\textsuperscript{64}
Nelson and Prezhdo demonstrated that hydroxylation lowers the band gap of graphene. However, the band gap of graphene was shown to be increased by epoxidation.68

The variation of the HOMO–LUMO energy gap for finite graphene (Gn), graphane (HGn), and fluorographene (FGn) models is presented in Figure 27.9.69 The HOMO–LUMO energy gap decreases with increasing the number of concentric hexagons for the model graphene-based systems. However, it does not converge to the periodic situation. Graphane shows a higher HOMO–LUMO energy gap than fluorographene, which has a considerably higher HOMO–LUMO gap than graphene. Although several instrumental techniques have been used, NMR characterization of graphene and chemically modified graphene systems (by covalent functionalization) has so far received much less attention. Through quantum chemical calculations, Vaara et al. have recently predicted NMR chemical shifts and shielding anisotropies as well as spin–spin couplings and anisotropies for graphene, graphane, and fluorographene. The three different model systems (graphene, graphane, and fluorographene) have been characterized with distinct 13C, 1H, and 19F NMR chemical shifts (Figure 27.9).69

27.5.3 MAGNETIC PROPERTIES

It is known that both graphene and graphane sheets are nonmagnetic (NM). Hydrogen addition or functionalization can induce magnetism in NM materials and can also change the magnetic configuration in some magnetic materials.32–35 Using DFT with GGA for exchange and correlation energy, Zhou et al. showed that semihydrogenated graphene is a ferromagnetic (FM) semiconductor.34 In their study, PBE functional for the GGA as implemented in VASP was used for calculations. The FM behavior of semihydrogenated graphene was explained by the presence of localized and unpaired electrons, which were generated by breaking of the delocalized π-bonding network of graphene in the process of half-hydrogenation, in the unhydrogenated carbon atoms. The magnetic moments at the unhydrogenated carbon sites coupled ferromagnetically with an estimated Curie temperature between 278 and 417 K, giving rise to an infinite magnetic sheet with structural integrity and magnetic homogeneity. Figure 27.10 shows three magnetic configurations: (1) FM coupling, (2) antiferromagnetic (AF) coupling, and (3) (NM
The calculation is spin unpolarized. The ground state of semihydrogenated graphene was found to be FM, which lies 0.15 and 0.49 eV lower in energy than that of the AF and NM states, respectively. Figure 27.10d and e shows the spin density plots with distribution of spins on semihydrogenated graphene.34 Graphene functionalized with oxygen atoms on one side and hydrogen atoms on the other side in the chair configuration was found to be an FM metal.33

Using a spin-polarized DFT method within the GGA, the PBE functional61 implemented in the Dmol3 package,62,63 Zeng and coworkers demonstrated that the magnetic moment and band gap of graphene can be tuned by selective hydrogenation.70 Figure 27.10 also shows the spin density distribution on selectively hydrogenated graphene and the dependence of the average magnetic moment per carbon atom at the edges on the side length of carbon triangles $n$ (for $m = 1$). The PBE functional61 implemented in the CASTEP program71 in Material Studio 4.1 package was used to compute optical absorption spectra of selectively hydrogenated graphene. The results of optical absorption spectra revealed that the side length of...
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27.5.4 Mechanical Properties

The mechanical properties of hydrogen-functionalized graphene have been investigated using quantum-mechanochemical reaction-coordinate (QMRC) simulations. The QMRC approach, which is implemented in DYQUAMECH software, was used to understand the origin of the mechanical anisotropy of graphene and making allowance for tracing a deformation-stimulated change in the chemical reactivity of both nanographene body and its individual atoms. Figure 27.11 shows the graphene and graphene that were considered for investigation of mechanical properties, and the stress–strain relationships for these systems. As shown in Figure 27.11a, the two sets distinguish two deformational modes that correspond to tensile deformation applied to armchair and zigzag edges of the sheets; these are called ac and zz modes. The hydrogenation effectively suppresses the tricotage-like pattern of the graphene deformation and failure. It is imperative to know that hydrogenation has a significant influence on the mechanical properties. Popova and Sheka demonstrated that the graphene deformation is mainly nonelastic, once rubbery high-elastic at the very beginning and plastic after reaching 4% (ac) and 2% (zz) strain. Young’s modulus (elastic parameter) is an important characteristic in studying mechanical properties. The reported values of Young’s moduli for (5,5) nanographene are 1.09 (ac mode) and 1.15 (zz mode) TPa. These values are significantly lowered (45%–55% reduction) by hydrogenation. QMRC simulations concluded that the tensile strength, fracture strain, and Young’s modulus are sensitive to the hydrogenation of graphene.

Peng et al. investigated the mechanical properties of graphene using DFT calculations that were performed with VASP. The stress–strain relationships were obtained by simulations carried out following three deformation modes: uniaxial strain in the zigzag direction (zigzag), uniaxial strain in the armchair direction (armchair), and equibiaxial strain (biaxial). Strain energy per atom was defined as $E_s = (E_{tot} - E_0)n$, where $E_{tot}$ is the total energy of the strained system, $E_0$ is the total energy of the strain-free system, and $n$ is the number of atoms in the unit cell. Figure 27.11 shows the plot of $E_s$ of graphene as a function of strain in uniaxial armchair (armchair), uniaxial zigzag (zigzag), and equibiaxial (biaxial) deformation. $E_s$ is seen to be anisotropic with strain direction. Furthermore, $E_s$ is nonsymmetrical for compression ($\eta < 0$) and tension ($\eta > 0$) for all three modes. Such nonsymmetry indicates the anharmonicity of the graphene structures. Peng et al. pointed out that the calculated Poisson ratio of uncoated carbon triangles can be controlled to adjust optical absorption properties of the quantum-dot array.
graphane is 0.078, which is about half of the corresponding value for graphene. Moreover, the value of 0.078 is the smallest among the discovered monolayer honeycomb structures. Elastic properties of hydrogenated graphene were explored by Colombo et al. using DFT calculations with the QUANTUM ESPRESSO package. Among the three configurations of graphane (chair-, boat-, or washboard-graphane), the chair-graphane exhibited both softening and hardening hyperelasticity, depending on the direction of the applied load.

27.5.5 **Charge Transfer, Vibrational Properties, and Specific Heat**

Graphene shows a moderate charge transfer from hydrogen to carbon (of the same order of magnitude as other hydrocarbons). Mulliken population analysis revealed a transfer of about 0.2 electronic charge in both chair and boat configurations. The highest frequency modes, corresponding to C–H bond stretching, occur at 3026 cm$^{-1}$ for the boat configuration.
and at 2919 cm\(^{-1}\) for the chair. The frequency is higher for the boat configuration due to the interaction between nearby hydrogen atoms on the same side of the plane. These C–H stretching modes are infrared active and should be useful in characterizing this compound.\(^{39}\) The electronic and optical properties of a PHG (C\(_2\)H-type) were investigated by means of the first-principles many-body Green’s function method. Strong charge-transfer excitonic effects were found to dominate the optical response of C\(_2\)H, giving rise to bound excitons. It was concluded that the PHG (C\(_2\)H-type) could be a promising candidate for the realization of the Bose–Einstein condensation because of the well-defined binding energy, longer lifetimes, and spatial separation of excitons.\(^{75}\)

Peelaers et al. studied the vibrational properties of graphene fluoride and graphane using \textit{ab initio} calculations with the ABINIT code. Experimental data of Raman peaks corresponding to fully hydrogenated and fully fluorinated graphene were confirmed by the \textit{ab initio} calculations. The specific heat of graphane was shown to be larger than the one for fully fluorinated graphene at high temperature.\(^{76}\) State-of-the-art nonadiabatic molecular dynamics (MD) combined with a time-dependent DFT study predicted that pure graphane has a very long nonradiative decay time (in the order of 100 ns). The electron coupling to the 1200 cm\(^{-1}\) vibrational mode was revealed to govern the nonradiative decay and luminescence line width of pure graphane.\(^{68}\)

### 27.5.6 Hydrogenation of Bilayer Graphene

BLG has received a great deal of attention recently. Samarakoon and Wang used DFT calculations to understand the electronic structural characteristics of fully and half (semi) hydrogenated chair and boat configurations of BLG (Figure 27.12a) under a perpendicular electric bias.\(^{77}\) Spin-polarized DFT with local density approximation (LDA) for exchange-correlation potential was utilized in their investigation. It is worth mentioning that the LDA approach is expected to provide qualitatively correct pictures and this technique remains the popular choice for investigations of electric field effects. GGA leads to weak bonding between graphene layers and yields excessively large values of bilayer distance. Therefore, LDA was suggested to be better than GGA. Similar to single layer fully hydrogenated graphene, the chair configuration was reported to be the lowest energy configuration for fully hydrogenated BLG (see the data in Table 27.4).\(^{77}\)

Samarakoon and Wang indicated that the band gap can be tuned and it is possible to change the semiconducting state to metallic by adjusting the bias voltage applied between the two hydrogenated graphene layers. The band gap decreases monotonically from 3.24 to 0 eV with increase of electric bias and the critical bias for the semiconducting to metallic transition is estimated to be 1.05 V/Å. As shown in Figure 27.12b, the charge density distributions are symmetrical in both conduction and valence bands in the absence of electric bias but the application of an electric bias induced charge accumulation and depletion in the conduction and valence bands, respectively. Desorption of hydrogen atoms from one layer of bilayer graphene in the chair configuration was demonstrated to produce an FM semiconductor with a tunable band gap. The semihydrogenated graphene of the chair configuration is an indirect band gap semiconductor with a small band gap and it is very different from graphene and graphane. The dependence of the spin-polarized bands of semihydrogenated BLG with positive and negative bias is shown in Figure 27.12c.\(^{77}\) Santos used first-principles electronic structure calculations to obtain knowledge on the magnetic moment induced by H atoms chemisorbed on the top layer of a few-layer (monolayer up to quadrilayer) graphene system and on how to tune the magnetic moment by the external electric field.\(^{78}\)

### 27.6 HIGHLIGHTS OF RECENT CRITICAL STUDIES RELATED TO GRAPHANE NANOSYSTEMS

Unzipping of SWCNTs by hydrogenation has been recently proposed as a possible road to preparation of graphene nanoribbons.\(^{43}\) The transport and magnetic properties of hydrogenated and other functionalized GNRs were studied using extensive first-principles calculations based on DFT.\(^{79}\) Computational investigation based on the DFT method concluded that the band gaps of GNRs decreased monotonically with an increase of ribbon width and were shown to be insensitive to the edge structure.\(^{80}\) Theoretical study on the transport properties of different sizes of hydrogenated graphene and GNRs has been reported recently, giving importance to the conductance fluctuation behavior in the localized regime.\(^{80}\) Leon and Pacheco investigated, using first-principles calculations, the electronic and dynamical properties of a molecular wire consisting of molecules with structures of graphane and with a GNR. Their study focused on understanding the behavior of the molecular wire, transmitting binary information without electric current.\(^{81}\) The electronic and magnetic properties of graphene nanoflakes (GNFs) were studied by controlling the hydrogen chemisorption on GNFs.\(^{82}\)

Using DFT computations, Li and Chen explored the structural and electronic properties of the experimentally known 2D patterned PHG with formula C\(_2\)H, one-dimensional (1D) C\(_2\)H nanotubes, and quasi-1D nanoribbons.\(^{83}\) The structure of the 2D layer has a wide band gap and similarly, all explored nanotube structures exhibit a wide band gap regardless of the tube diameter and chirality. However, quasi-1D GNRs were predicted to be either of metallic or semiconducting nature depending on the chirality and edge configuration.\(^{85}\) Wen et al. have computationally explored the stability and band gap of graphene nanotubes of both zigzag and armchair types. They revealed that the band gap increases on reducing the diameter of the graphene nanotubes.\(^{86}\) The narrow GNRs could be readily obtained from wide GNRs by partial hydrogenation as reported based on the spin-polarized DFT calculations.\(^{85}\) Since many potential applications of graphane and graphane-based systems require interaction with aqueous media, Vanzo et al. investigated, by means of large-scale MD simulations, the wettability of graphane and...
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Functionalized graphane by alkyl groups of increasing chain lengths. Previous important studies related to graphane nanosystems are listed in Table 27.5.

Information regarding theoretical and experimental studies on fluorinated graphene can be obtained from recent reviews. Hu et al. have investigated the structural stability, and the electronic and magnetic properties of fluorinated BLG. It is not our goal to provide details about fluorinated BLG. However, we would like to highlight one particular characteristic—the structural stability. The chair configuration is found to be energetically more stable than the boat form for the fully fluorinated BLG whereas two different configurations were reported to be energetically favored for the half fluorinated BLG. Sivek et al. investigated, using DFT calculations, the stability and electronic properties of fluorinated BLG (bilayer fluorographene) and compared the results obtained for bilayer graphene. Bilayer fluorographene was found to be more stable than bilayer graphene and is almost as strong as graphene.

**FIGURE 27.12** (a) Side and top views of the structures of fully hydrogenated as well as semihydrogenated chair and boat conformations of bilayer graphene. Carbon atoms on top and on bottom layers are colored with light gray and dark gray, respectively. Hydrogen atoms are colored with small white. (b) Calculated dependence of band gap on perpendicular applied electric bias for the bilayer graphane in chair configuration: (i) no bias, (ii) 0.39 V/Å electric bias, and (iii) 1.03 V/Å electric bias. Insets: extracted charge density distribution at the band center (Γ point) of the corresponding conduction and valence band states. The isovalue is 0.025 au. (c) Calculated band gaps of semihydrogenated chair structure with (i) 0.26 V/Å electric bias, (ii) no bias, and (iii) 0.39 V/Å electric bias. Insets: extracted spin density distribution at the band center (Γ point) of the corresponding conduction and valence band states. The isovalue is 0.025 au. (Reprinted with permission from Samarakoon, D. K., and Wang, X.-Q. Tunable band gap in hydrogenated bilayer graphene. *ACS Nano*, 4, 4126–4130. Copyright 2010 American Chemical Society.)

**TABLE 27.4**

<table>
<thead>
<tr>
<th>Structure</th>
<th>$E_b$ (eV)</th>
<th>$E_g$ (eV)</th>
<th>$l$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fully hydrogenated chair</td>
<td>−12.00</td>
<td>3.24</td>
<td>1.54</td>
</tr>
<tr>
<td>Fully hydrogenated boat</td>
<td>−11.93</td>
<td>2.92</td>
<td>1.54</td>
</tr>
<tr>
<td>Semihydrogenated chair</td>
<td>−10.55</td>
<td>0.54</td>
<td>1.65</td>
</tr>
<tr>
<td>Semihydrogenated boat I</td>
<td>−10.79</td>
<td>2.35</td>
<td>1.63</td>
</tr>
<tr>
<td>Semihydrogenated boat II</td>
<td>−10.85</td>
<td>0.50</td>
<td>3.26</td>
</tr>
</tbody>
</table>


Note: Labels I and II refer to boat configurations with and without interlayer bonding, respectively.
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27.7 POTENTIAL APPLICATIONS

The unique mechanical properties of graphene will facilitate high-speed charge and discharge of hydrogen atoms. Therefore, the graphene–graphane systems could be used to build advanced high speed and efficient hydrogen storage devices. Sofo et al. predicted that the volumetric hydrogen capacity of 0.12 kg H₂/L is higher than the DOE target of 0.081 kg H₂/L for the year 2015. Furthermore, the gravimetric capacity of 7.7 wt.% hydrogen is higher than the 6 wt.% hydrogen of DOE target for 2010. Therefore, an important potential application of graphane is as a source of hydrogen fuel. Boukhvalov et al. reported values of 0.53 eV (25.5 kJ/mol) and 0.42 eV (20.3 kJ/mol) correspondingly for the chemisorption energy per hydrogen atom for a single hydrogen pair and for fully hydrogenated graphene. The latter value is close to the experimental result of 19.6 kJ/mol for hydrogenated nanotubes. It should be highlighted that the above-mentioned values appear to be quite reasonable in view of potential applications of graphene for hydrogen storage. Also, alkali metal–graphane complexes were investigated for their potential of hydrogen storage. Recent computational investigations using state-of-the-art first-principles DFT and MD simulations have revealed that a reasonably high H₂ storage capacity of 12.12 wt.% could be obtained with 25% of Li doping on a graphene sheet. The adsorption energies of H₂ on lithium-functionalized graphane were found to be within the ideal range of 0.15–0.20 eV. Therefore, lithium-functionalized graphane could be suitable for practical hydrogen storage applications. Polyliithiated (OLi₂) functionalized graphane is expected to be a fascinating material for high-capacity H₂ storage (~12.90 wt.%) based on first-principles calculations.

The tunable gaps between mid-ultraviolet and near-infrared regions (ca. 0.5–5 eV) in hydrogenated graphene may lead to potential applications in future electronics and photonics (e.g., solar cells). Certain partially hydrogenated GNRs with a band gap around 1.5 eV were predicted to be ideal materials for solar cell absorbers due to the high carrier mobility. Graphane nanoribbons are anticipated to have promising applications in optics and opto-electronics due to the wide band gap. The holes formed by the H vacancies on the graphene surface provide ideal doping sites, which may lead to novel graphene-based semiconductors with n-type doping (deposited with alkali metals or alkaline-earth metals) or spin injection (deposited with magnetic transition metals). Functionalized graphane and transition-metal-atom-embedded graphane are expected to be promising materials for high-performance 2D spintronic devices. Graphane and its derivatives have the potential to replace conventional semiconductors in electronics, catalysis, and energy applications, greatly reducing device size and power consumption. The chemically patterned (by hydrogenation of) graphene can be viewed as an array of semiconducting quantum dots, where the hydrogenated carbon stripes play the role of quantum confinement. Hydrogenated graphene-based quantum dots may be used in light-emitting devices.

Computational study indicated that graphanes could be excellent candidates for semiconductor applications compared to carbon nanotubes and nanoribbons. Graphene nanostructures could form efficient molecular wires. Since graphene has a small Poisson ratio, it is predicted to be a good candidate to build tubes or pipelines that can transfer materials with high speed by applying high pressure. The nanotubes made with graphene will be very stable under working conditions due to the negative coupling between the Poisson ratio and applied stress. The graphene bilayer has an interesting feature of tunable band gap, which paves the way for new electronic devices, from lasers that change color to electronic circuits that can rearrange themselves. It may also be useful to develop an FM semiconductor by removal of hydrogen from one layer.

27.8 SUMMARY

Different possible conformers of graphene (fully hydrogenated graphene), their preparation, characterization, and electronic, magnetic, and mechanical properties are covered in this chapter. Two-dimensional hydrocarbon derivative of graphene (graphane) is experimentally known. Chair and boat configurations of fused cyclohexane rings were predicted to be energetically favorable for graphene. Advanced experimental techniques were employed to produce partially and fully hydrogenated graphene. Two important techniques are atomic hydrogen beam and exposure to hydrogen-based plasmas. Other techniques for preparation of hydrogenated graphene include e-beam lithography and Birch-type reduction. Hydrogenation of graphene on different surfaces as well as on multilayer graphene has been reported experimentally. Raman spectroscopy has been mainly used besides SEM, XPS, STM, STS, etc. for characterization of hydrogenated graphene. Experimental evidence for ortho and para addition of two hydrogen atoms for low H coverage on graphene, and controlled hydrogenation of graphene are available in the literature.

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Graphene is a zero band gap semimetal but the hydrogenation induces the band gap. We have highlighted how to tune the transport properties of graphene by varying the H coverage, and the temperature dependence of the electronic transport properties of hydrogenated graphene. We have discussed different theoretical methods employed to study the reactivity of graphene for hydrogenation (low coverage), stability of partially and fully hydrogenated graphene, and variation of band gap by changing the hydrogen coverage. Computational Raman, IR, and NMR spectroscopy data are provided. Hydrogen addition to graphene induces magnetism and the semihydrogenated graphene was reported to be FM. The tensile strength, fracture strain, and Young’s modulus were demonstrated to be sensitive to the functionalization of graphene by hydrogen atoms. Recent studies of experimentally realized fluorographene and PHG (C,H) are specifically mentioned along with hydrogenated BLG, bilayer fluorographene, and hydrogenated nanotubes. Finally, we have revealed the potential applications of hydrogenated graphene.

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